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Canadian Intellectual Property Office

Ottawa Hull K1A 0C9

(21) (A1) 2,122,882
(22) 1994/05/04
(43) 1994/11/06

(51) INTL.CL.[5] C10G-007/10

(19)(CA) **APPLICATION FOR CANADIAN PATENT** (12)

5,089,5/96

(54) Neutralizer for Corrosion Control

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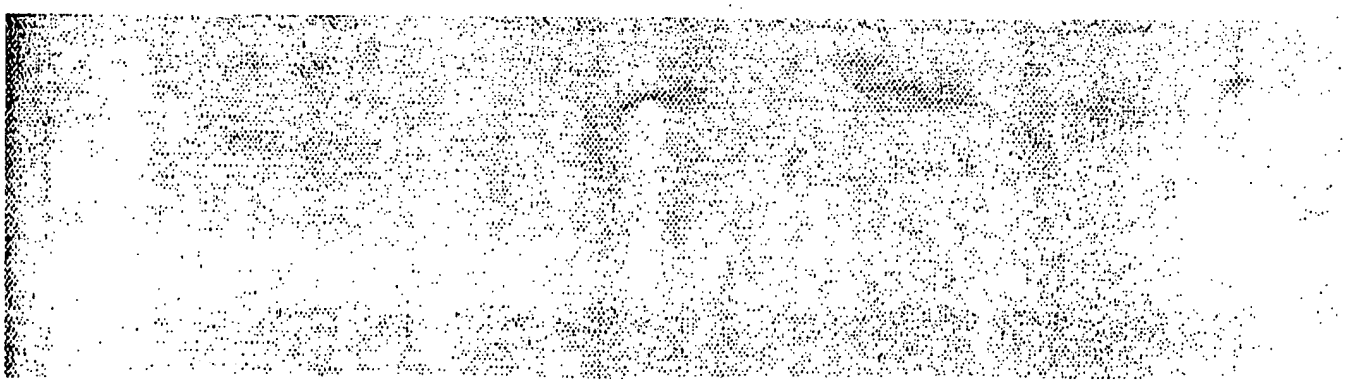
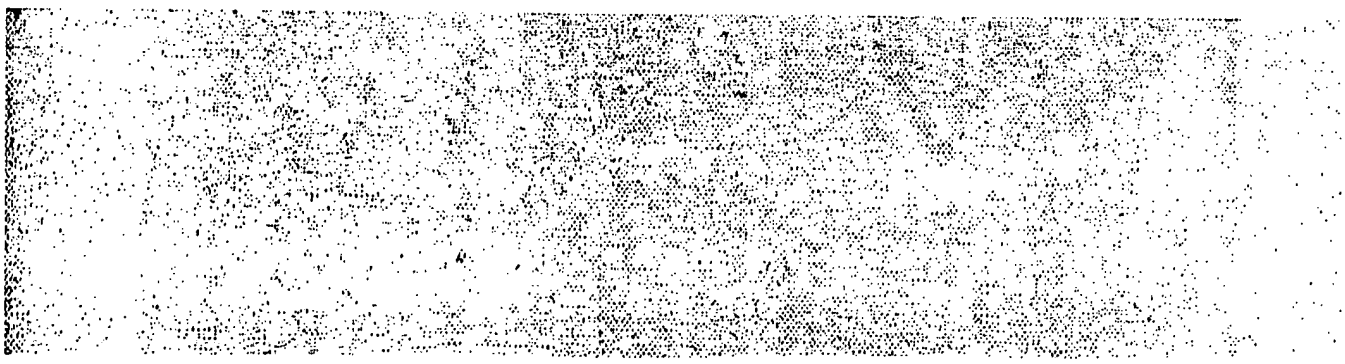
(30) (US) 08/058,969 1993/05/05

(57) 26 Claims



ABSTRACT OF THE DISCLOSURE

Highly advantageous corrosion control can be provided in the overhead systems of crude oil distillation units through the use of 2-ethyl hexylamine and tert-alkyl amines having greater than 7 but less than 14 carbon atoms. These amines are generally liquid, and the amine salts formed when the amines are contacted with access acid are soluble in both aqueous and hydrocarbon phases.



Attorney Docket No. 3207
vndmac/PA/DR6/97

NEW NEUTRALIZER FOR CORROSION CONTROL

This application relates to methods and compositions useful in reducing corrosion in the distillation units of crude oil refining systems. More specifically, the subject matter of this application relates to processes for neutralizing acid components in the overhead systems of crude petroleum distillation units.

The addition of neutralizing and film-forming amines has been proposed to replace ammonia and caustic as neutralizers in crude oil refining, particularly in the distillation columns and related heat exchanger bundles and associated distillation equipment. Organic amines, specifically the low-boiling aliphatic primary and secondary amines the salts of which remain stable at refinery distillation temperatures, have been demonstrated to be useful in this regard. At times, however, plugging and fouling of the distillation column has resulted, presumably as a result of untimely precipitation and/or the development of poorly soluble complexes and emulsions produced in the neutralization process. Several proprietary amine mixtures have been proposed to overcome these problems, as has the use of "polyamines" and long chain molecules having highly polar end groups and oleophilic groups on the chain. These proposals have met with some positive success. Nevertheless, corrosion continues to be a persistent problem in the refining and distillation of crude and heavy hydrocarbons.

SUMMARY OF THE INVENTION

The present invention is based upon the discovery that highly advantageous corrosion control can be provided in the overhead systems of crude oil distillation units through the use of certain branched chain alkyl amines, including 2-ethyl hexylamine and tert-alkyl amines with from 10 to 14 carbon atoms. Accordingly, the present invention is directed to a method for reducing corrosion in the overhead systems of crude petroleum distillation units which comprises injecting into the process flow

upstream from the region of corrosion concern an effective amount of a branched chain alkyl amines having at least eight carbon atoms.

According to one aspect of the present invention there is provided a process for reducing corrosion in the overhead systems of a crude petroleum distillation unit by neutralizing excess acid present in a hydrocarbon vapor stream, where the temperature of said hydrocarbon vapor stream is between 240°F and 300°F comprising the steps of: injecting into said distillation unit an effective amount of a branched chain alkyl amine, having at least eight carbon atoms, selected from the group consisting of 2-ethyl hexylamines, tert-alkyl amines having from 10-14 carbon atoms, and mixtures thereof; wherein said alkyl amine is further characterized in that salts with hydrochloric and other strong acids are soluble in both phases.

According to a further aspect of the present invention there is provided a process for reducing acid salt corrosion in the overhead systems of crude petroleum distillation units comprising: injecting into the process flow upstream from the region of concern an effective amount of a branched chain alkyl amine characterized in that the alkyl amine group has at least seven carbon atoms and the amine salt formed when the alkyl amine reacts with acid components in the distillation unit flow stream is liquid at the reaction conditions, has reduced corrosivity in both liquid and hydrocarbons as compared to acids and other acid salts and is soluble in both hydrocarbon and water under conditions ambient in the overhead systems.

According to another aspect of the present invention there is provided a process for reducing corrosion in the overhead systems of a crude petroleum distillation unit by neutralizing excess acid present in a hydrocarbon vapor stream, where the temperature of said hydrocarbon vapor stream is between 240°F and 300°F comprising the steps of: injecting into said distillation unit an effective amount of tert-alkyl amines having from 10-14 carbon atoms wherein said alkyl amine is further characterized in that salts with hydrochloric and other strong acids are soluble in both phases.

According to a still further aspect of the present invention there is provided a process for reducing acid salt corrosion in the overhead systems of crude petroleum distillation units comprising: injecting into the process flow upstream from the region of concern an effective amount of tert-alkyl amines having from 10-14 carbon atoms; wherein the amine salt formed when the alkyl amine reacts with acid components in the distillation unit flow stream is liquid at the reaction conditions, has reduced corrosivity in both liquid and hydrocarbons as compared to acids and other acid salts, and is soluble in both hydrocarbon and water under conditions ambient in the overhead systems.

According to another aspect of the present invention there is provided a process for reducing corrosion in the overhead systems of a crude petroleum distillation unit by neutralizing excess acid present in a hydrocarbon vapor stream, where the temperature of said hydrocarbon vapor stream is between 240°F and 300°F comprising the steps of: injecting into said distillation

unit an effective amount of PRIMENE® 81-R upstream from the point of corrosion concern; wherein said alkyl amine is further characterized in that salts with hydrochloric and other strong acids are soluble in both phases.

According to a further aspect of the present invention there is provided a process for reducing acid salt corrosion in the overhead systems of crude petroleum distillation units comprising: injecting into the process flow upstream from the region of concern an effective amount of PRIMENE® 81-R characterized in that the amine salts formed when the PRIMENE® 81-R reacts with acid components in the distillation unit flow stream are liquid at the reaction conditions, has reduced corrosivity in both aqueous and hydrocarbon phases as compared to acids and other acid salts, and is soluble in both aqueous and hydrocarbon phases under conditions ambient in the overhead systems.

According to yet another aspect of the present invention there is provided a process for reducing corrosion in the overhead systems of a crude petroleum distillation unit by neutralizing excess acid present in a hydrocarbon vapor stream, where the temperature of said hydrocarbon vapor stream is between 240°F and 300°F comprising the steps of: injecting into said distillation unit an effective amount of 2-ethyl hexylamine; wherein said alkyl amine is further characterized in that salts with hydrochloric and other strong acids are soluble in both phases.

According to a still further aspect of the present invention there is provided a process for reducing acid salt

corrosion in the overhead systems of crude petroleum distillation units comprising: injecting into the process flow upstream from the region of concern an effective amount of 2-ethyl hexylamine characterized in that the amine salt formed when the 2-ethyl hexylamine reacts with acid components in the distillation unit flow stream is liquid at the reaction conditions, has reduced corrosivity in both liquid and hydrocarbons as compared to acids and other acid salts, and is soluble in both hydrocarbon and water under conditions ambient in the overhead systems.

In some preferred features: said alkyl amine is of the formula $R\text{-}NH_2$, wherein R is a branched alkyl group of greater than seven but less than fourteen carbon atoms; the branched alkyl amine is injected by spraying the branched alkyl amine into said hydrocarbon vapor stream; said excess acid is comprised of hydrochloric acid and hydrogen sulfide; the branched chain alkyl amine has from eight to fourteen carbon atoms; and the injecting of the alkyl amine is achieved by spraying the branched chain alkyl amines into the crude unit overhead vapor stream at a point upstream of the area of corrosion concern where temperatures are between 240°F and 300°F.

2-Ethyl hexylamine and tert-alkyl amines with from 10 to 14 carbon atoms may be characterized generally as neutralizing amines which are completely soluble in the heavier hydrocarbon phase which passes through a crude unit distillation operation. Most importantly, the effective amines are further characterized in that the amine salts formed by reaction of the amines with acidic components in the distillation flow stream are sufficiently

soluble at the process conditions that they do not precipitate, complex, form emulsions, or otherwise interact to produce thick, fouling materials.

The branched chain alkyl amines preferred for use in the methods of the present invention have limited solubility in water and a condensation point higher than that of water under the conditions present in the overhead distillation systems. More importantly, and unpredictably, the amine salts that form when these branched chain alkyl amines react with acid components in the flow stream are also liquid at the reaction conditions and further are soluble in both hydrocarbon and water phases under the conditions ambient in the overhead distillation systems.

DETAILED DESCRIPTION OF THE INVENTION

Specific branched chain alkyl amines that have been found acceptable for use in the method of the present invention include 2-ethyl hexylamine and tert-alkyl amines with from 10 to 14 carbon atoms. A preferred tert-alkyl amine is a commercially available, proprietary product called PRIMENE® 81-R, sold in this country by the Rohm and Haas Co. of Philadelphia, Pennsylvania. According to MSDS information provided by that company, PRIMENE® 81-R is a non-volatile liquid amine consisting of greater than 75% by weight C12 -C14 tert-alkyl amines and less than 25% by weight C11 and smaller tert-alkyl amines.

A preferred formulation of 2-ethyl hexylamine is a commercially available, proprietary product called ARMEEN® L8D, sold in this country by

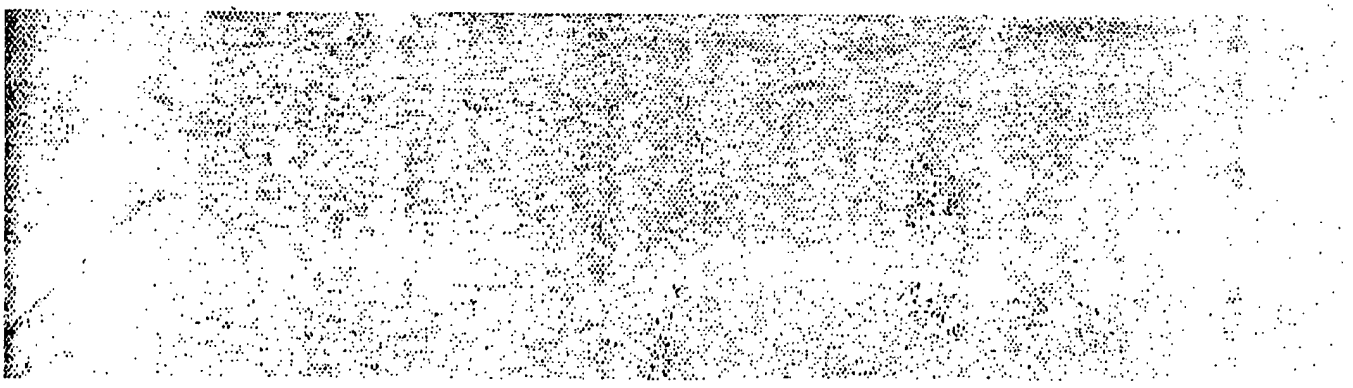
AKZO Chemicals, Inc. According to MSDS information provided by that company, ARMEEN® L8D is a non-volatile liquid amine consisting of greater than 98% by weight 2-ethyl-1-hexanamine (2-ethyl hexylamine) and less than 2% by weight 2-ethyl-N-(2-ethylhexyl)-1-hexanamine.

It has been found that the amine salts produced when these amines are introduced to an acidic environment have reduced corrosivity in both liquid and hydrocarbon phases as compared to salts formed by most other amines. Most importantly, these amine salts are completely soluble/miscible in hydrocarbon and do not cause water-in-oil emulsions. These characteristics make the amine salts of the present invention highly useful in controlling corrosion.

These branched chain alkyl amines may be used alone, or in combination. They may also be used in combination with one or more semi-volatile lighter amines, including alkanol- and alkoxy-amines.

The amine solution should be injected into the process flow stream at an appropriate point upstream from the location where corrosion is a problem. Typically, the amine solution will be diluted with a heavy hydrocarbon material and injected directly into the overhead vapors of the distillation column. In order for the amine to be fully atomized, it is preferred to inject it into a slip stream employing a thin, tapered nozzle (a "quill"). Alternatively, but less preferably, the amine solution may be injected into the crude unit tower as part of the column charge, or into the reflux line.

The amount of branched chain alkyl amine used should be effective to reduce the corrosion at the area of concern. As will be understood by those skilled in this art, that amount will depend upon a number of factors, including the nature and amount of acid components existing in the hydrocarbon flow stream, the amount of water that exists in the overhead distillation systems and the type of corrosion which is the problem. It has been found helpful to measure the pH at the accumulator and employ sufficient amine to produce a pH between about 5 to 7 at that location.



The primary consideration will be the effect on the corrosion of concern, and that will require a reasonable amount of experimentation.

DISCLOSURE

To confirm the solubility and corrosivity characteristics of the branched chain alkyl amines and their respective salts, the following laboratory tests were carried out.

Example 1: HCl gas was bubbled through 60g of neat PRIMENE® 81-R, employing an excess of HCl over that calculated to fully react with the amine. The liquid soon became very viscous. A drop of this liquid placed on indicator paper showed that the pH was in the basic range. To assure that the reaction continued to completion, 100ml of hexane was added and more HCl was bubbled through. After the reaction was determined fully complete, the hexane solvent was removed in a rota-vap aspirator vacuum and the residue viscous liquid was further dried under a high vacuum. Weight of the final product was 71.2g.

Example 2: The amine/salt product formed by the procedure in Example 1 was dissolved in kerosene at approximately 150°C to form a 10% weight to volume (W/V) solution. When the salt dissolved, the liquid immediately became brownish in color and became darker upon heating. A mild steel corrosion coupon was placed in this solution. The initial weight of this coupon was 8.4551g. Forty-five minutes after introducing the coupon, the solution was slightly agitated by slowly bubbling nitrogen gas through the solution. This was continued for approximately 5 hours, during which the temperature of the solution was maintained in the range 147°C to 157°C. Agitation was stopped, and the coupon removed and weighed approximately six hours after it was placed in the solution. The final weight was 8.4387g, indicating a total weight loss of 16.4mg and an overall corrosion rate of 70MPY.

Example 3: Employing a similar procedure to that of Examples 1 and 2 with ARMEEN® L8D, the overall corrosion rate in kerosene at 150°C was determined to be 451MPY.

Example 4: The amine/salt product obtained by the procedure of Example 1 was introduced into deionized water to form a 10% weight to volume (W/V) solution. The solution was heated to boiling, until the salt was completely dissolved, at which point a corrosion coupon was introduced into the solution. The corrosion coupon had an initial weight of 8.4096g. The solution was mechanically stirred and maintained at boiling temperature (approximately 101°C) for six hours, after which it was removed and weighed. The final weight was 8.3478g, indicating a weight loss of 61.8mg and a corrosion rate equal to 265MPY. The pH of the final solution was measured at 6.3.

Example 5: Employing a procedure similar to that of Example 4, above, corrosivity data was obtained for a series of aqueous amine/HCl salt solutions. The results are shown in Table 1, below:

TABLE 1

AMINE	CORROSION RATE (MPY) (2M solution)
Allyl amine	396
Diallyl amine	366
Furfuryl amine	739
(2-Ethyl-Oxazoline)	1590
PRIMENE® 81-R	440
ARMEEN® L8D	364

Example 6: To determine whether the amine salts produced with the tert-alkyl amines of the present invention will cause emulsification in the presence of water and hydrocarbon, 438mg of PRIMENE® 81-R - HCl salt made according to the procedure of Example 1 was added to 44ml of ISOPAR E, a commercial hydrocarbon having density of 0.702g per milliliter. This measured out to approximately 10mg of the amine salt per milliliter of hydrocarbon. Water was added and the container capped and shaken twenty-five times by hand and the mixture then allowed to settle. No emulsion was observed. In like manner, various mixtures of ISOPAR E

and water were formed, roughly in a volume ratio of 90/10, containing from 25ppm to 500ppm of the tert-alkyl amine salt produced according to the procedure of Example 1. These mixtures were shaken in the same manner as above and allowed to settle. No severe emulsions were observed and the liquids separated readily.

Example 7: To determine the extent to which the tert-alkyl amine salt dissolves in the hydrocarbon and aqueous phases, 25ml of a solution of the tert-alkyl amine in ISOPAR E was combined with 25ml of deionized water and equilibrated at room temperature by gently stirring with a magnetic stir bar and allowing to stand overnight. The aqueous phase was then removed with a pipette and 5.0ml aliquots were analyzed for chlorides by mercurimetric titration. In repeating examples, it was concluded that approximately 87 to 90% of the amine salt was dissolved in the water, the remainder staying in solution with the hydrocarbon.

Example 8: Employing a procedure similar to that of Example 7, above, the extent to which 2-ethyl hexylamine salts derived from Armeen® L8D dissolve in the hydrocarbon and aqueous phases was determined. Approximately 99.5% of the amine salt was dissolved in the water while the remaining 0.5% stayed in solution with the hydrocarbon phase.

It will be understood that modifications of the procedures described in the foregoing examples can be made without parting from the scope and spirit of the invention.

What is claimed is:

1. A process for reducing corrosion in the overhead systems of a crude petroleum distillation unit by neutralizing excess acid present in a hydrocarbon vapor stream, where the temperature of said hydrocarbon vapor stream is between 240°F and 300°F comprising the steps of:

injecting into said distillation unit an effective amount of a branched chain alkyl amine, having at least eight carbon atoms, selected from the group consisting of 2-ethyl hexylamines, tert-alkyl amines having from 10-14 carbon atoms, and mixtures thereof;

wherein said alkyl amine is further characterized in that salts with hydrochloric and other strong acids are soluble in both phases.

2. A process as recited in claim 1 wherein said alkyl amine is of the formula $R\text{-}NH_2$, wherein R is a branched alkyl group of greater than seven but less than fourteen carbon atoms.

3. A process as recited in claim 1 wherein the branched alkyl amine is injected by spraying the branched alkyl amine into said hydrocarbon vapor stream.

4. A process as recited in claim 1 wherein said excess acid is comprised of hydrochloric acid and hydrogen sulfide.

5. A process for reducing acid salt corrosion in the overhead systems of crude petroleum distillation units comprising:

injecting into the process flow upstream from the region of concern an effective amount of a branched chain alkyl amine characterized in that the alkyl amine group has at least seven carbon atoms and the amine salt formed when the alkyl amine reacts with acid components in the distillation unit flow stream is liquid at the reaction conditions, has reduced corrosivity in both liquid and hydrocarbons as compared to acids and other acid salts and is soluble in both hydrocarbon and water under conditions ambient in the overhead systems.

6. A process as recited in claim 5 wherein the branched chain alkyl amine has from eight to fourteen carbon atoms.

7. A process as recited in claim 5 wherein the injecting of the alkyl amine is achieved by spraying the branched chain alkyl amines into the crude unit overhead vapor stream at a point upstream of the area of corrosion concern where temperatures are betweeen 240°F and 300°F.

8. A process for reducing corrosion in the overhead systems of a crude petroleum distillation unit by neutralizing excess acid present in a hydrocarbon vapor stream, where the temperature of said hydrocarbon vapor stream is between 240°F and 300°F comprising the steps of:

injecting into said distillation unit an effective amount of tert-alkyl amines having from 10-14 carbon atoms wherein said alkyl amine is further characterized in that salts with hydrochloric and other strong acids are soluble in both phases.

9. A process as recited in claim 8 wherein the alkyl amine is injected by spraying the tert-alkyl amines into said hydrocarbon vapor stream.

10. A process as recited in claim 8 wherein said excess acid is comprised of hydrochloric acid and hydrogen sulfide.

11. A process as recited in claim 9 wherein the tert-alkyl amine PRIMENE® 81-R.

12. A process for reducing acid salt corrosion in the overhead systems of crude petroleum distillation units comprising:

injecting into the process flow upstream from the region of concern an effective amount of tert-alkyl amines having from 10-14 carbon atoms;

wherein the amine salt formed when the alkyl amine reacts with acid components in the distillation unit flow stream is liquid at the reaction conditions, has reduced corrosivity in both liquid and hydrocarbons as compared to acids and other acid salts, and is soluble in both hydrocarbon and water under conditions ambient in the overhead systems.

13. A process as recited in claim 12 wherein the injecting of the branched chain alkyl amine is achieved by spraying the tert-alkyl amines into the crude unit overhead vapor stream at a point upstream of the area of corrosion concern where temperatures are betweeen 240°F and 300° F.

14. A process as recited in claim 12 wherein the tert-alkyl amine PRIMENE® 81-R.

15. A process for reducing corrosion in the overhead systems of a crude petroleum distillation unit by neutralizing excess acid present in a hydrocarbon vapor stream, where the temperature of said hydrocarbon vapor stream is between 240°F and 300°F comprising the steps of:

injecting into said distillation unit an effective amount of PRIMENE® 81-R upstream from the point of corrosion concern;

wherein said alkyl amine is further characterized in that salts with hydrochloric and other strong acids are soluble in both phases.

16. A process as recited in claim 15 wherein the PRIMENE® 81-R is injected by spraying the PRIMENE® 81-R into said hydrocarbon vapor stream.

17. A process as recited in claim 15 wherein said excess acid is comprised of hydrochloric acid and hydrogen sulfide.

18. A process for reducing acid salt corrosion in the overhead systems of crude petroleum distillation units comprising:

injecting into the process flow upstream from the region of concern an effective amount of PRIMENE® 81-R characterized in that the amine salts formed when the PRIMENE® 81-R reacts with acid components in the distillation unit flow stream are liquid at the reaction conditions, has reduced corrosivity in both aqueous and hydrocarbon phases as compared to acids and other acid salts, and is soluble in both aqueous and hydrocarbon phases under conditions ambient in the overhead systems.

19. A process as recited in claim 18 wherein the injecting of the PRIMENE® 81-R is achieved by spraying the PRIMENE® 81-R into the crude unit overhead vapor stream at a point upstream of the area of corrosion concern where temperatures are betweeen 240°F and 300°F.

20. A process for reducing corrosion in the overhead systems of a crude petroleum distillation unit by neutralizing excess acid present in a hydrocarbon vapor stream, where the temperature of said hydrocarbon vapor stream is between 240°F and 300°F comprising the steps of:

injecting into said distillation unit an effective amount of 2-ethyl hexylamine;

wherein said alkyl amine is further characterized in that salts with hydrochloric and other strong acids are soluble in both phases.

21. A process as recited in claim 20 wherein the 2-ethyl hexylamine is injected by spraying the 2-ethyl hexylamine into said hydrocarbon vapor stream.

22. A process as recited in claim 20 wherein said excess acid is comprised of hydrochloric acid and hydrogen sulfide.

23. A process as recited in claim 20 wherein the 2-ethyl hexylamine is ARMEEN® L8D.

24. A process for reducing acid salt corrosion in the overhead systems of crude petroleum distillation units comprising:

injecting into the process flow upstream from the region of concern an effective amount of 2-ethyl hexylamine characterized in that the amine salt formed when the 2-ethyl hexylamine reacts with acid components in the distillation unit flow stream is liquid at the reaction conditions, has reduced corrosivity in both liquid and hydrocarbons as compared to acids and other acid salts, and is soluble in both hydrocarbon and water under conditions ambient in the overhead systems.

25. A process as recited in claim 24, wherein the injecting of the 2-ethyl hexylamine is achieved by spraying the 2-ethyl hexylamine into the crude unit overhead vapor stream at a point upstream of the area of corrosion concern where temperatures are betweeen 240°F and 300°F.

26. A process as recited in claim 24 wherein the 2-ethyl hexylamine is ARMEEN® L8D.

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